Electrocatalysis of the SiC Particle-Modified Glassy Carbon Electrode for the Oxidation of Adrenaline

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The electrocatalytic properties of the SiC particle-modified glassy carbon electrode (MGC) for adrenaline oxidation were studied by cyclic voltammetry (CV), double-potential step chronocoulometry (DPSCC), and electrochemical impedance spectroscopy (EIS) techniques in McIlvaine buffer solution. It was shown that the electrode modified with SiC particles markedly displayed an electrocatalytic effect on the process of the electrochemical reaction of adrenaline, i.e., the activity and the reversibility of the MGC electrode has been significantly improved. This was attributed to the adsorption effect of the electroactive adrenaline molecules on the MGC electrode surface.

Keywords: Adrenaline; SiC; Glassy carbon; Electrocatalysis.

INTRODUCTION

Adrenaline is known to be an important hormone secreted by the medulla of the adrenal glands and also serves as a chemical mediator for conveying the nerve pulse to efferent organs.[1-2] It belongs to a group of compounds known as catecholamines, which play a particularly important role in the regulation of physiological processes in living systems. Catecholamines serve as carriers for the nervous system, influencing the constriction of blood vessels and controlling tissue metabolism by increasing the levels of glucose and lactic acid.[3-4] Adrenaline can be studied directly by electrochemical methods because of its similar structure to *o*-dihydroxybenzene, and the group of -CH(OH)- at α carbon leading to easily giving out electrons. After Hawley's first study on electrochemical reaction of adrenaline at a carbon paste electrode,[1] the electron transfer nature of adrenaline has been extensively studied.[2-7]

The electrode processes of an electroactive species is in close relation to the electrode surface pretreatment.[8-9] Various well-established and novel surface modification procedures were used on a glassy carbon (GC) electrode to yield specific surface states,[10-12] since a GC electrode is easier to be modified than other solid electrodes.[12-13]

There are several different surface-modifying ways for improving electrocatalytic activity of an electrode, such as solid particle adhering, covalent bonding, adsorption, polymer-coating, and electrochemical activating, etc. Among these, the solid particle modification is a simple and effective method.[14-16] Recently, we found the SiC particle-modified GC electrode possesses good electrocatalytic activity for organic compounds with π electrons. In this article, we present the results of our studies on the electrocatalytical effect of a SiC particle-modified GC electrode for adrenaline oxidation in McIlvaine buffer solution by CV, DPSCC, and EIS techniques.

EXPERIMENTAL

The reagent of adrenaline (> 97%) is bought form Fluka Co. (Sweden). The concentration of adrenaline aqueous solution is 2.50×10^{-3} mol L^{-1}. Other solutions used were prepared with analytic grade reagents and doubly distilled water. The $6^{\#}$ Al_2O_3 polishing paper and $2000^{\#}$ SiC polishing paper used were purchased from Shanghai Emery Co. (China).

The three-electrode-system was used to carry out electrochemical tests. A glassy carbon electrode serves as a working electrode, a platinum wire serves as a counter electrode, and a saturation calomel electrode (SCE) serves as reference

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electrode. A Luggin capillary was used to connect the reference and working electrodes. Highly pure nitrogen gas was used to remove oxygen dissolved in solution before measurements, and all measurements were carried out under nitrogen atmosphere at room temperature (24 ± 2 °C). All potentials reported are in respect to SCE.

The glassy carbon electrode has been polished using 6# Al_2O_3 polishing paper till a mirror-like surface was obtained. Then it was ultrasonically washed with double distilled-water for at least 20 min, and dried in air. A so treated electrode is called fresh no-treated electrode, denoted as bare GC.

A pretreated glassy carbon electrode, which is denoted as MGC, was obtained after the electrode had been modified with SiC particles by polishing with SiC emery paper. The area of the bare GC and MGC electrodes is 0.132 cm^2 and 0.180 cm^2, respectively, which were measured by CV tests[9] with different scan rates (30, 50, 80, 100 mV s^{-1}) in 5 mmol L^{-1} $K_3Fe(CN)_6$ + 0.5 mol L^{-1} KCl solution, and calculated with a diffusion coefficient D of 7.65 × 10^{-6} cm^2 s^{-1} for $Fe(CN)_6^{3-}$.[9]

The electrochemical experiments were performed using an electrochemical impedance system (EG&G PAR) including a model 283 potentiostat/galvanostat and a model 1025 lock-in amplifier, which were controlled by the EG&G PARC Power CV and Power Sine softwares on an IBM computer. For EIS measurements, a 10 mV (rms) amplitude sine wave was applied to the electrode under potential static control and the frequency range was from 0.01 Hz to 100 kHz. During EIS measurement, the electrode potential was kept at the value of the open circuit potential. The impendence results were analyzed with the program of EQUIVCRT written by Boukamp.[17]

DPSCC measurements were designed with potential step magnitudes that were large enough to ensure that any electroreactant diffuses to the electrode at its maximum rate. At t = 0 s, the potential is stepped from E_i to E_f, where adrenaline is oxided under diffusion-limited condition. That potential is enforced for a period τ then the electrode is returned to E_i. For the experiments performed in pH 4.5 McIlvaine buffer solution, E_i equals -0.3 V and E_f equals 1.0 V, while for that in pH 2.5 buffer solution, E_i = -0.2 V and E_f = 1.0 V, respectively.

RESULTS AND DISCUSSION

Cyclic voltametry

Electrochemistry of adrenaline is in close relation to solution pH values, i.e., when pH < 2, electrooxidation of adrenaline only leads to formation of adrenalinequinone, but when pH > 2, a series of subsequent chemical and electrochemical reactions would occur.[1-3,5]

Fig. 1 is the voltammetry response of adrenaline at GC and MGC electrodes in a McIlvaine buffer solution with pH 4.5. Three peaks are shown in Fig. 1. Among them peak 1 (1′) and 2 (2′) are the reoxidation peaks of adrenaline/adrenalinequinone redox couple. Peak 3 (3′) corresponds to the electroreduction of adrenaline into leucoadrenochrome; peak 4 (4′) means the leucoadrenochrome produced at the electrode surface is electro-oxidized into adrenochrome. Peak 5 (5′) corresponds to the electrochemical oxidation of 5,6-dihydroxyl-N-methylindole which is the dehydrated product of adrenaline.[3,5,18]

From Fig. 1, it can be seen that on the GC electrode, the potential separation between peak 1 and 2 is about 350 mV, and that between peak 3 and 4 is 60 mV. The curve is flat with relatively lower peak currents. The results indicate that the electrocatalytic activity is weak. On the MGC electrode, there are also five peaks presented (see Fig. 1, solid line), but the position and features of redox peaks in CV curve change remarkably. It can be seen that the oxidation peaks shift negatively and the reduction peaks shift positively, leading to decrease of the separations between peak 1′ and 2′, and between peak 3′ and 4′ by about 320 mV and 30 mV, respectively, which correspond to a well improved reversibility of the electrochemical processes for adrenaline at the MGC electrode surface. It also can be seen that the redox peaks become higher and sharper, indicating that the oxidation-reduction current is raised markedly.

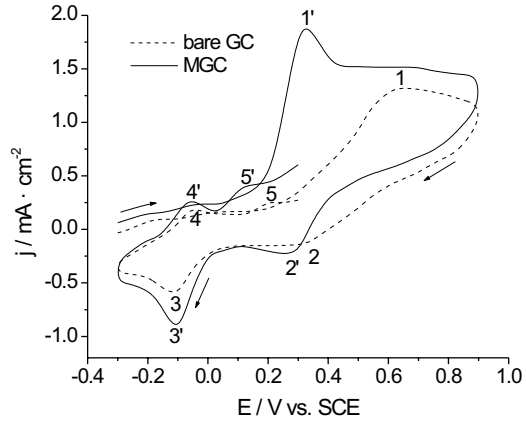

Fig. 1. Cyclic voltammograms of adrenaline at bare GC and MGC electrodes, in pH 4.5 McIlvaine buffer solution with 6.0 mmol L^{-1} adrenaline. ν = 50 mV s^{-1}.

In pH 2.5 McIlvaine buffer solution (Fig. 2), the CV result is similar to that obtained in pH 4.5 solution. At a bare GC electrode, the peak-to-peak separation between peak 1 and 2 is 0.59 V, but at MGC electrode, that between peak 1′ and 2′ becomes 0.10 V. Meanwhile, the peak currents at MGC are about twice as much as those at a bare GC electrode. All of the above results clearly indicate the electrocatalytic effect of the SiC-particle modified GC electrode.

Adsorption of adrenaline on surface of electrode

The double potential step is very powerful in identifying adsorption phenomena by chronocoulometry.[19-20] For a large forward potential step at a planar electrode and considering an oxidation, the current caused by a potential step is given by the Cottrell equation. And by integrating current to stepping time, we arrive at[9,19]

$$Q = 2\,n\,F\,A\,C\,D^{1/2}\,\pi^{-1/2}\,f(t) + Q_{dl} + Q_{ads} \qquad [1]$$

where Q_{dl} is capacitive electric quantity used to charge Helmholtz double layer on the surface of electrode; Q_{ads} is the charge resulting from the electroactive species which are adsorbed over the electrode surface; and f(t) is a function of stepping time. For the forward potential step, $f(t) = t^{1/2}$, and for the backward potential step, $f(t) = \tau^{1/2} + (t - \tau)^{1/2} - t^{1/2}$. The other symbols have their usual meanings. Therefore, a plot of Q vs. f(t) is linear with an intercept at Q axis, which corresponds to the sum of Q_{dl} and Q_{ads}. Q_{dl} can be determined from the intercept of the plot of Q vs. $t^{1/2}$ which was obtained in corresponding bottom solution (i.e. without electroactive species). Further more, from Q_{ads}, the surface excess, Γ can be calculated according to[9,19]

$$Q_{ads} = n\,F\,A\,\Gamma \qquad [2]$$

By DPSCC, we investigated the adsorption of adrenaline on untreated and pretreated GC electrodes. The typical Q-f(t) plots are shown in Fig. 3, which are the results of chronocoulometric response to double potential step for adrenaline measured using MGC electrode in pH 2.5 McIlvaine buffer solution. From Fig. 3, it can be seen that the intercept differences between straight lines (1) and (2), and between (3) and (4), are not zero, indicating the occurence of adsorption of adrenaline and its oxided products on the electrode surface. So the surface excess, Γ, for adrenaline on MGC in pH 2.5 McIlvaine buffer solution was determined as 12.79×10^{-10} mol/cm^{-2} according to equation [2].

For comparison, DPSCC measurements were carried out using both GC and MGC electrodes and in pH 4.5 and pH 2.5 McIlvaine buffer solutions, respectively, and the results are listed in Table 1. From Table 1, it can be seen that the amount of adsorption of adrenaline on MGC (~1.25×10^{-9} mol cm^{-2}) is much larger than that on bare GC (~1.23×10^{-10} mol cm^{-2}), indicating that the electroactivity of the MGC electrode is well improved by SiC particle modification and that the remarkable adsorption of electroactive adrenaline on MGC could account for the distinctly increasing reversibility for the electrode processes as shown in CV measurements

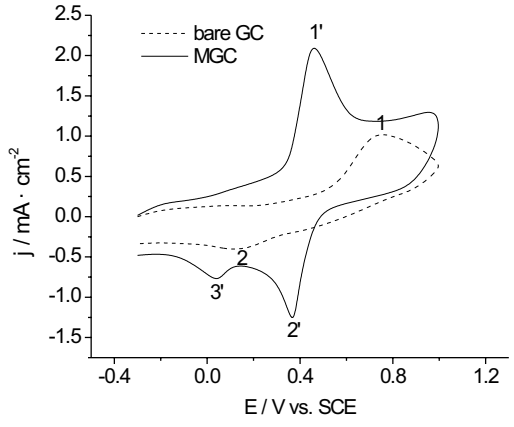

Fig. 2. Cyclic voltammograms of adrenaline at bare GC and MGC electrodes, in pH 2.5 McIlvaine buffer solution with 6.0 mmol L^{-1} adrenaline. ν = 50 mV s^{-1}.

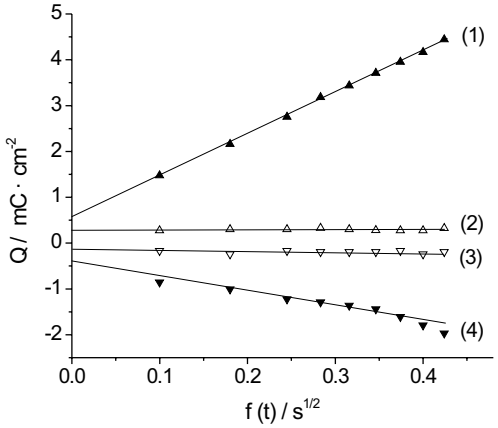

Fig. 3. Q-f(t) plots of chronocoulometric response of adrenaline at the MGC electrode, which were obtained by forward potential step (▲) and reverse step (▼) in pH 2.5 McIlvaine buffer solution with 6.0 mmol L^{-1} adrenaline, and by forward potential step (△) and reverse step (▽) in pH 2.5 McIlvaine buffer solution without adrenaline, respectively. The range of potential steps is from -0.2 V to 1.0 V.

Table 1. Q-f(t) plot parameters obtained from DPSCC measurements with bare GC and MGC electrodes in McIlvaine buffer solutions containing 6 mmol L^{-1} adrenaline

Electrodes	pH	Intercept difference for forward step/10^{-6} C cm^{-2}	Intercept difference for backward step/10^{-6} C cm^{-2}	10^{10} Γ/mol cm^{-2}
bare GC	2.5	25.68	24.02	1.33
	4.5	19.85	19.24	1.13
MGC	2.5	246.83	222.94	12.79
	4.5	239.44	223.28	12.43

(Figs. 1 and 2).

EIS Measurements

EIS technology is a useful tool for studying surface processes on an electrode.[5,9] We investigated the impedance behavior of adrenaline using both GCE and MGCE electrodes, both in pH 4.5 and in pH 2.5 McIlvaine buffer solutions, respectively. Fig. 4 shows the impedance spectrum in a Nyquist presentation obtained at both bare GC and SiC particle modified MGC electrodes in pH 4.5 McIlvaine buffer solution containing 6 mmol L^{-1} adrenaline.

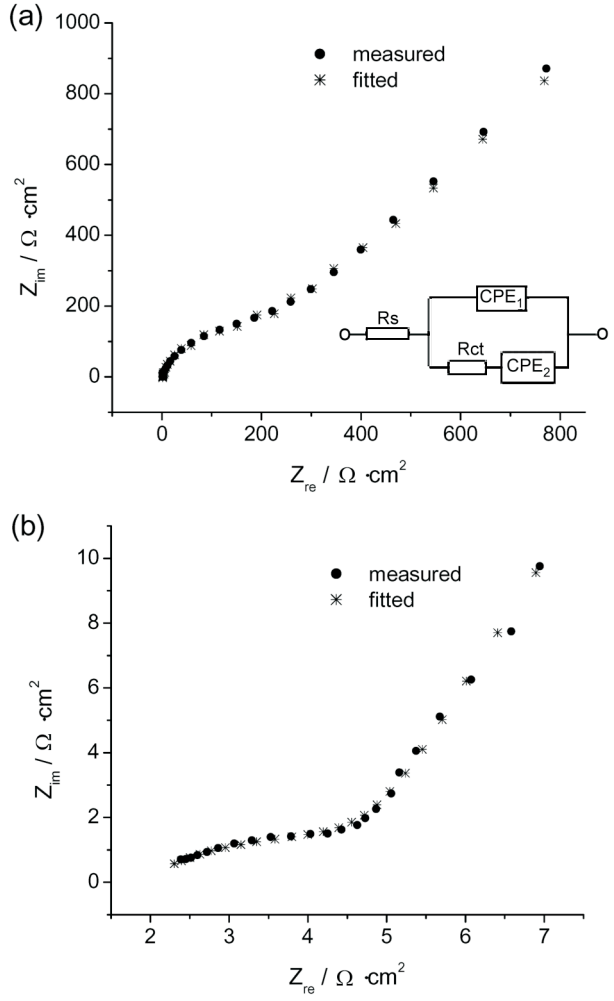

Fig. 4. Complex-plane plot of the impedance of the bare GC electrode (a) and SiC particles modified MGC electrode (b) in pH 4.5 McIlvanine buffer solution with the presence of 6 mmol L^{-1} adrenaline.

Considering the existence of adrenaline adsorption on the electrode surface, an equivalent circuit was proposed and used to model the measured impedance data, which is presented as the insertion in Fig. 4a. Where, R_s is the solution resistance; R_{ct} is the charge-transfer resistance. Since the dispersing effect[21-23] exists for the electrochemical system of GC/solution studied, the constant phase element (CPE) was used instead of the ideal capacitor in every fit in order to improve the final fit and minimize error. CPE_1 corresponds to the double-layer capacitance at the electrode/solution interface, and CPE_2 is both related to the diffusion process of the electroactive species to and from the electrode surface, and related to the surface adsorption of the electroactive species. The complex impedance of a CPE is defined as

$$Z_{CPE} = \frac{1}{Y_0}(j\omega)^{-n} \qquad [3]$$

where $j = (-1)^2$, ω is the angular frequency, Y_0 is a constant and n may vary between -1 and 1. In some specific cases where n = 1, 0.5, 0, -1, a CPE represents a pure capacitor, a semi-infinite Warburg element, a pure resistor, and a pure inductor, respectively.

From Fig. 4, we can see that the plot consists of a depressed arc at high frequencies and a straight line at low frequencies, involving one time constant. The simulated plots based on the model agree well with the measured ones, revealing the equivalent circuit used is reasonable.

All simulated results, including that obtained in pH 2.5 McIlvaine buffer solution, are presented in Table 2. The most significant characteristic of the EIS results as shown in Table 2 is that the electron transfer resistance (R_{ct}) measured at

Table 2. Electrochemical impedance spectroscopy measurement results with GC and MGC electrodes in McIlvaine buffer solutions containing 6 mmol L^{-1} adrenaline

Electrodes	pH	10^4 Y_1/Ω^{-1} cm^{-2} s^n	n_1	R_2/Ω cm^2	10^3 Y_2/Ω^{-1} cm^{-2} s^n	n_2
bare GC	2.5	1.28	0.90	180.8	1.22	0.61
	4.5	1.29	0.89	253.4	1.20	0.60
MGC	2.5	3.04	0.69	3.91	3.02	0.75
	4.5	3.01	0.68	4.55	3.07	0.76

MGC electrodes is much lower than that measured at bare GC electrodes both in pH 4.5 and in pH 2.5 solutions, indicating the SiC particle modified MGC electrode processes high electrocatalytic ability for the oxidation reaction of adrenaline. This is in good agreement with the results obtained from CV measurements as shown above.

After polishing treatment of the GC electrode on SiC emery paper, the SiC abrading particles adhering to the GC base electrode may play a role of modifying the electrode surface and act as the "bridge" for exchanging electrons between electroactive species (adrenaline, as in this work) and the GC substrate. Since SiC belongs to the group of covalence solids, the carbon atoms and silicon atoms at the surface have unbonded sp3 hybrid orbitals, which is an advantage for linking with covalent electroactive ions or molecules. The amount of defects on the surface of the electrode also increases with polishing. Since it has been demonstrated that[13] the surface defects have a high level of reaction activity, the amount of the defects can directly influence the electron transfer rate and the degree of adsorption of electroactive species on an electrode.

CONCLUSIONS

By using CV, DPSCC and EIS techniques, the electrocatalytic properties for adrenaline oxidation of the SiC particle-modified glassy carbon electrode were investigated in McIlvaine buffer solutions. It was demonstrated that comparing with bare GC electrodes, the peak-to-peak potential separation and the charge transfer resistance (R_{ct}) for the oxidation of adrenaline were significantly decreased on the MGC electrode, while the adsorption amount of adrenaline molecules on MGC was one order of magnitude higher than that on bare GC. The electrocatalytic activity and reactive reversibility of the MGC electrode were obviously enhanced by the surface modification pretreatment. These findings could be helpful for the minimum detection and analysis of adrenaline in the human body.

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